Thermodynamic constraints on reflectance reciprocity and Kirchhoff's law

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Contrary to common belief, neither reciprocity of the bidirectional reflectance distribution function (BRDF) nor the directional form of Kirchhoff's electromagnetic radiation law can be demonstrated on the basis of energy conservation. The BRDF is generally considered reciprocal as an extension of Helmholtz reciprocity, but Helmholtz reciprocity does not always hold. We describe the flaw in a thermodynamic demonstration of reciprocity that uses an enclosure calculation. Some conclusions can be drawn from the enclosure calculation, but reciprocity requires more restrictive conditions. We conclude that, although they can be violated, reciprocity and the directional form of Kirchhoff's law generally hold because of the quantum-mechanical principle of time-reversal invariance, which applies to most materials.

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1. Introduction

Optical reflectance reciprocity is a property of a material or a structure. In particular, it applies when a source of light is reflected off a material and detected. If reciprocity holds for the material, the detector response is the same when the source and the detector positions are switched. The validity of reciprocity is of interest, for example, in statistical physics, radiative heat transfer, and radiometry. In these disciplines, it is generally accepted that reciprocity holds for a large class of materials and systems. This paper is the result of one of us (Li) questioning the enclosure calculation argument for reciprocity in a popular heat transfer text by Siegel and Howell.[1] Such thermodynamic arguments appear to be flawed, and as a result we sought to demonstrate the flaw in the reasoning and to determine under what conditions reciprocity should hold. In radiometry, reciprocity is manifested most fundamentally as reciprocity of the bidirectional reflectance distribution function (BRDF). For our application, reciprocity is important for BRDF measurements[2] and for BRDF models.[3] The issue of whether reciprocity holds also has consequences for other optical properties of a material, such as the various relations among directional and hemispherical reflectivity, emissivity, and absorptivity. Of particular interest is the equivalence of the directional absorptivity and the directional emissivity, which is the directional form of Kirchhoff's law. These issues are developed furthest in the field of statistical physics, so it is useful to connect some of the results in that field to radiometry, which is our main concern here.

The BRDF, defined by Nicodemus *et al.*,[4] is a fundamental characterization of material reflectance. Further, under normal conditions, it is a property only of the material, and it is independent of the material temperature and the incident radiation field. The BRDF is defined for infinitesimal solid angles, but it can be measured as an average value over small, finite angles. Other measurable optical properties may be obtained by integration of the BRDF over larger incident and reflected solid angles. These properties include biconical reflectance factors and directional emissivities and absorptivities. In fact, many such properties are defined in terms of the BRDF. For monochromatic light with a specific polarization, the BRDF is a four-dimensional function of the incident and the reflected zenith and azimuth angles. Usually, the BRDF is taken to be reciprocal, meaning that the

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value is the same when the incident and the reflected angles are switched:

$$f(\theta_i, \phi_i; \theta_j, \phi_j) = f(\theta_j, \phi_j; \theta_i, \phi_i). \qquad (1)$$

Here the first two angles correspond to the incident direction and the last two to the reflected direction. The basis for this relation is an extension to diffuse reflection of the Helmholtz optical reciprocity theorem.[5] Helmholtz stated his theorem of reciprocity in 1874. A corrected version of an early translation to English is provided by Clarke and Parry[6] in an experimental treatment of the issue for reflectometry. The statement asserts that when the behavior of light can be approximated as a scalar wave, there is an equal output angular flux density for a given input flux density when the direction of propagation is reversed. The asymmetrical properties of the magneto-optical effect were discovered earlier by Faraday, in 1845, and Helmholtz excluded systems with this behavior.[7] Such systems violate Helmholtz reciprocity because they are not invariant under time reversal.

In the 1930's, L. Onsager showed that with irreversible systems, such as scattering media, the quantum-mechanical reversibility at the microscopic scale can lead to macroscopic reciprocity relations in a variety of situations. The Onsager reciprocity relations may be applied to support optical reciprocity. Microscopic reversibility means that at atomic scales, for a particular geometry, wavelength, and polarization state, the probability of an interaction is the same as that of its reverse.[8] For an unpolarized source and a detector that is insensitive to polarization, this microscopic time-reversal symmetry means that the intensity registered by the detector that is reflected off some physical system in the geometric far field is the same when the source and the detector positions are switched.[9]

It is straightforward to show that the reciprocity of the detected intensity in that situation is equivalent to the reciprocity of the BRDF when the system in question is an element of a flat surface or of a structured surface that is measured under appropriate averaging conditions. We consider structured surfaces that can have both transmitting and opaque-reflecting elements in an arrangement that, at some scale and measurement distance, is equivalent to a flat surface for the purposes of defining the optical properties. In any case, the system must be invariant under time reversal for this reciprocity to apply. But in fact it is easy to devise a system that is not invariant under time reversal. One such surface has elements that are Faraday isolators. The Faraday isolator is a dielectric in a strong magnetic field that rotates polarization asymmetrically for the two directions of travel. When this is placed between polarizers, the transmission is asymmetrical. Time-reversal symmetry dictates that the field be reversed for the opposite direction of travel, and if it is not, reciprocity is violated. With a Faraday isolator, if not a flat surface, then at least a structured surface that violates BRDF reciprocity at some particular pair of angles can be constructed.[10,11]

Faraday rotation is a weak effect, even for optimal materials in a strong magnetic field. In fact, in the absence of a strong field, time-reversal symmetry and thus reciprocity apply to most materials. Measurement error is probably the dominant cause of nonreciprocal behavior in experiments. For instance, one report of measured reciprocity failure with roughened glass and aluminum[12] was later discredited as caused by uncontrolled factors.[13,14]

Although it appears that the assumption of microscopic time reversal is the most general basis for reciprocity, there are special cases for which it may be shown to hold without invoking time reversal. For instance, if the material is isotropic, nonconducting, and nonmagnetic, it is straightforward to show by the Fresnel equations that the reflectance and the transmission at an interface are reciprocal. Reciprocity is also supported by the Fresnel–Kirchhoff diffraction formula,[15] and another study shows that the Lorentz theorem leads to reciprocal electromagnetic scattering by obstacles.[16] In fact, for structures of opaque and transmitting materials that are reciprocal, it may be shown that the average BRDF of the structure is reciprocal.[10] Additional cases in which reciprocity can be shown to apply without invoking time reversal are discussed by Shelankov and Pikus.[9]

On the other hand, it appears that reciprocity cannot be derived on the basis of the conservation of energy, as it is applied in an enclosure calculation. To begin with, this is evident from the fact that reciprocity can be violated, yet there are no known violations of the thermodynamic laws. We will demonstrate analytically that maintaining the equilibrium conditions in an enclosure does not require BRDF reciprocity, although this has been claimed in the literature. For example, Nicodemus[17,18] questioned Bauer's version of this argument[19] but did not demonstrate the flaw in Bauer's reasoning. Our contribution is to demonstrate the flaw in a contemporary example of the erroneous argument put forth in Siegel and Howell's text.[1]

2. Flawed Thermodynamic Argument

The supposed thermodynamic argument employs an enclosure calculation. This is a common method for demonstrating some conservation-of-energy properties, especially in the field of radiative heat transfer. The enclosure has perfectly black, absorbing inside walls, is isolated from the surroundings, and is in equilibrium. Under these conditions, it can be shown that if the statistical fluctuations are time averaged, the radiation inside the enclosure is isotropic, and it can also be shown that the temperature of all elements is the same.

For the purposes of this discussion, there is no loss in generality in shaping the black enclosure as a unit hemisphere with a black bottom plane, and no loss in generality by taking an element of interest, dA_f, to be at the center of the bottom plane. This familiar arrangement is shown in Fig. 1. This unit hemisphere

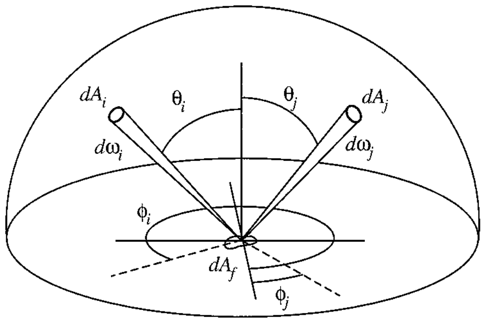

Fig. 1. Geometry definitions for the BRDF on the unit hemisphere.

enclosure simplifies the subtended solid angles and distances involved in the calculations. Further, a radiating element on the unit hemisphere, dA_i, and the corresponding element of the solid angle are related by

$$\frac{\mathrm{d}\omega}{\mathrm{d}A_i} = \frac{1}{R^2} = 1. \tag{2}$$

Finally, other elements on the bottom plane have zero projected area with respect to the element of interest at the center, and so they do not appear in the calculations, but they do contribute to the isotropic radiation field in the enclosure.

In this isothermal enclosure, the time-averaged net heat flow into and out of any element must total zero. Otherwise the nonzero net flow would change the temperature of the element. Here the radiant flux is the only mechanism for heat flow. In addition to the zero total flux, it turns out that for an all-black enclosure, the flux exchange between any two elements dA_i and dA_j on the enclosure surface is zero. This flux comprises two parts. First, the reflected flux exchange between two elements is zero. This is because there are no reflections when there are only black elements in the enclosure. Second, the direct flux exchange between two elements is zero. This is true for any two black elements at the same temperature and at any orientation because of a straightforward radiometric property called shape factor reciprocity.[20] This is not related to reflectance reciprocity. Thus, in summary, for the all-black enclosure, the net flux at one element must be zero and the net exchange between any two elements is zero.

Now, the erroneous argument with a nonblack element goes as follows: Replace the black element at dA_f with a nonblack element that has an arbitrary BRDF that is possibly not reciprocal. It is argued that, because this new nonblack element does not influence the direct exchange between the two black elements that we already had, dA_i and dA_j, this exchange must still be zero, which we said was true because of shape factor reciprocity. Then, it is argued falsely that, because the total exchange between dA_i and dA_j must still be zero to maintain equilibrium, the reflected exchange must also be zero. If it were determined that the reflected exchange is, in fact, zero, it can be shown that reciprocity must hold. The total radiant exchange between two black elements through an arbitrary nonblack element, however, is no longer necessarily just the direct flux and the reflected flux. The flux from the nonblack element towards one of the black elements must still be the same as the isotropic flux in the all-black enclosure, but this flux can consist of flux reflected from any part of the enclosure, as well as flux absorbed from any part of the enclosure and then emitted. This leads to a myriad of possibilities for a nonreciprocal BRDF that satisfy the equilibrium requirements. In Section 3, we present one of these as an example.

3. Reciprocity Violation

Recall that no matter what the BRDF of dA_f, all elements including dA_f must be at the same temperature, and the net flux out of any element must be zero. Consider the exchange between any black element, dA_j, and the nonblack element of interest, dA_f. We have said that the direct flux exchange between two black elements is zero by shape factor reciprocity. So we can say that, because both the summed net flux exchange between a given black element, dA_j, and all other black elements is zero and the net flux out of dA_j is zero, the flux exchange between dA_j and dA_f must also be zero. In other words, the nonblack element at dA_f must have the same spectral radiance in all directions as a black element. From this we can equate the flux between dA_f and dA_j in opposite directions. All of the flux from dA_j is emitted, but some of the flux returning from dA_f is emitted and some is reflected from the hemisphere.

The flux Φ in terms of radiance L from an element is

$$d^2\Phi = L d\omega dA \cos\theta. \tag{3}$$

Here $d\omega$ is the elemental solid angle subtended by a source with radiance L, and θ is the zenith angle with respect to the normal of the receiving area element dA. The BRDF may be defined as the ratio of the radiance in direction j to the irradiance in the plane of the element from the direction i:

$$f(\theta_i, \phi_i; \theta_j, \phi_j) = \frac{dL_j}{dE_i}. \tag{4}$$

For the flux from the center nonblack element, dA_f, in the direction of one of the black elements, dA_j, there are two parts, the flux reflected from the hemisphere and the flux emitted thermally. The flux reflected by dA_f from any black element, dA_i, on the unit hemisphere that arrives at dA_j is given by

$$d^3\Phi = f(\theta_i, \phi_i; \theta_j, \phi_j) dA_f \cos\theta_j dA_j L_b dA_i \cos\theta_i. \tag{5}$$

Here L_b is the blackbody radiance, which has a fixed value for a single temperature and wavelength. This flux may be integrated over all elements on the hemisphere to get the total reflected portion toward dA_j:

$$d^2\Phi = \int_{2\pi} f(\theta_i, \phi_i; \theta_j, \phi_j) dA_f \cos\theta_j dA_j L_b \mathrm{d}\Omega_i, \quad (6)$$

for which $dA_i \cos\theta_i$ becomes the projected solid angle element $\mathrm{d}\Omega_i = \cos\theta_i \sin\theta_i \mathrm{d}\theta_i \mathrm{d}\phi_i$. The flux emitted thermally by dA_f toward dA_j is simply

$$d^2\Phi = \varepsilon(\theta_j, \phi_j) L_b dA_f dA_j \cos\theta_j. \quad (7)$$

The total flux from dA_f to any element dA_j is thus the sum,

$$d^2\Phi = \int_{2\pi} f(\theta_i, \phi_i; \theta_j, \phi_j) dA_f \cos\theta_j dA_j L_b \mathrm{d}\Omega_i + \varepsilon(\theta_j, \phi_j) L_b dA_f dA_j \cos\theta_j. \quad (8)$$

Straightforward radiometry gives the total flux from a black element dA_j of blackbody radiance L_b that arrives at the nonblack element dA_f. It is

$$d^2\Phi = L_b dA_f dA_j \cos\theta_j. \quad (9)$$

We have said that Eqs. (8) and (9) must be equal between the nonblack element and any black element. This holds true between the nonblack element and each of the two black elements also, which is the basis of the next part of the derivation. Using this fact, we present a special case in which the BRDF is not reciprocal but in which the thermodynamic enclosure calculation axioms still hold. Note that there are many possibilities, and this is just a simple case to illustrate the preceding discussion.

For brevity, let the BRDF $f(\theta_i, \phi_i; \theta_j, \phi_j)$ be denoted $f(i, j)$ and the emissivity $\varepsilon(\theta_j, \phi_j)$ be $\varepsilon(j)$. Next, convert the area elements to small finite angles. If both Eqs. (8) and (9) are integrated over some small finite solid angle Ω_a and we cancel $L_b dA_f$, we have for our thermodynamic balance between dA_f and the area subtended by a small solid angle Ω_a,

$$\int_{\Omega_a} \mathrm{d}\Omega_j = \int_{\Omega_a}\int_{2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega_a} \varepsilon(j)\mathrm{d}\Omega_j. \quad (10)$$

Similarly, for some other small solid angle in another direction Ω_b,

$$\int_{\Omega_b} \mathrm{d}\Omega_j = \int_{\Omega b}\int_{2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega b} \varepsilon(j)\mathrm{d}\Omega_j. \quad (11)$$

For convenience, simplify the geometry by letting Ω_a and Ω_b have an arbitrary shape but be such that

$$\int_{\Omega_a} \mathrm{d}\Omega_j \equiv \int_{\Omega_b} \mathrm{d}\Omega_j \equiv k, \quad (12)$$

and the thermodynamic equality constraint becomes

$$\int_{\Omega_a}\int_{2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega_a} \varepsilon(j)\mathrm{d}\Omega_j = \int_{\Omega b}\int_{2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega b} \varepsilon(j)\mathrm{d}\Omega_j. \quad (13)$$

Our aim is to show that this can be satisfied with nonreciprocal BRDF. Because integration is linear, we can separate the reflection term into two parts. For the left-hand side,

$$\int_{\Omega_a}\int_{2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j = \int_{\Omega_a}\left[\int_{\Omega_b} f(i, j)\mathrm{d}\Omega_i + \int_{\Omega_b\backslash 2\pi} f(i, j)\mathrm{d}\Omega_i\right]\mathrm{d}\Omega_j. \quad (14)$$

Here the domain of integration $\Omega_b\backslash 2\pi$ denotes the solid angle region that is the complement of the domain Ω_b with respect to the hemisphere. The symbol is borrowed from set notation and is not division or subtraction. For convenience, we set the integrals over these larger domains to be equal for the example,

$$\int_{\Omega_a}\int_{\Omega_b\backslash 2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j \equiv \int_{\Omega_b}\int_{\Omega_a\backslash 2\pi} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j. \quad (15)$$

We then have a relation between emissivity and BRDF that must hold for the two solid angles,

$$\int_{\Omega_a}\int_{\Omega_b} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega_a} \varepsilon(j)\mathrm{d}\Omega_j = \int_{\Omega_b}\int_{\Omega_a} f(i, j)\mathrm{d}\Omega_i \mathrm{d}\Omega_j + \int_{\Omega_b} \varepsilon(j)\mathrm{d}\Omega_j. \quad (16)$$

Next, we took the BRDF and the emissivity to be constant inside the small solid angles Ω_a and Ω_b so that we could bring the BRDF and the emissivity outside the integrals. Note that the difference in the sequence of integration in the BRDF terms in the preceding expression is the reason for the different order of the arguments in the BRDF terms in what follows.

$$f(b, a)\int_{\Omega_a} \mathrm{d}\Omega_j \int_{\Omega_b} \mathrm{d}\Omega_i + \varepsilon(a)\int_{\Omega_a} \mathrm{d}\Omega_j = f(a, b)\int_{\Omega_b} \mathrm{d}\Omega_j \int_{\Omega_a} \mathrm{d}\Omega_i + \varepsilon(b)\int_{\Omega_b} \mathrm{d}\Omega_j. \quad (17)$$

So finally, if the BRDF were not reciprocal for this pair of angles, we could still satisfy the thermodynamic equilibrium requirements, but we must have the following relation between the BRDF disparity

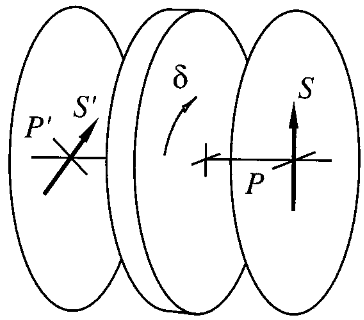

Fig. 2. Form of the Faraday isolator. The S polarization is rotated to line up with the S' polarization for right-to-left propagation. For left-to-right propagation, the S' is rotated to the P polarization and is blocked.

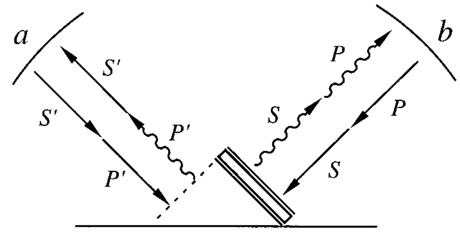

Fig. 3. Structured system that violates reciprocity and the directional form of Kirchhoff's law. Straight arrows show radiation from the cavity walls that has not been absorbed by the isolator. The wavy arrows show the radiation emitted by the isolator. The S polarization from the b branch reflects without being absorbed with an S' polarization toward the a branch. The P polarization from the b branch and both the S' and P' polarizations from the a branch are absorbed by the isolator.

and the directional emissivity disparity for average values over the regions a and b,

$$\varepsilon(\theta_a, \phi_a) - \varepsilon(\theta_b, \phi_b) = k[f(\theta_a, \phi_a; \theta_b, \phi_b) - f(\theta_b, \phi_b; \theta_a, \phi_a)]. \quad (18)$$

Recall that k is a geometric constant that was defined in Eq. (12). In summary, we began with the thermodynamic axioms for an isothermal enclosure and concluded that there can be a disparity in the BRDF between the two directions when there is a commensurate difference in the angular emissivity.

It fact, in an isothermal enclosure, a Faraday isolator with absorbing polarizers would violate reciprocity in this manner and the isotropic radiation field would be maintained. Figure 2 depicts an ideal isolator that consists of a dielectric element in a magnetic field. We take the isolator to be fully transmitting and to have a field strength such that the polarization of light is rotated 45°, but asymmetrically, in the direction δ, regardless of the direction of travel. The element is sandwiched between two ideal linear polarizers rotated to a relative angle of 45°. This means that half the light travels from right to left, but no light is transmitted from left to right. A polarizing filter can absorb or reflect the blocked polarization. For this example, let us take the polarizers to absorb the blocked polarization state fully. The emissivity for these elements is therefore unity for the blocked polarization and zero for the transmitted polarization.

Under these conditions it is easy to calculate the balance of emitted, absorbed, and reflected light for a reflecting configuration in equilibrium in an isotropic radiation field. Figure 3 illustrates this result. The lower boundary is a perfect specular reflector. The straight arrows represent light from the cavity walls that has not been absorbed by the isolator, and the wavy arrows are light radiated thermally from the isolator. In traveling from b to a, the S-polarization component from the cavity wall is transmitted and rotated to S'. The P polarization is absorbed by the first polarizer along that direction of travel. On the other hand, in traveling from a to b, both the S'- and P'-polarization components from the cavity wall are absorbed by the isolator. The P' component is absorbed by the first polarizer, and the S' component is absorbed by the second polarizer in the a to b direction. Not only does this configuration violate reciprocity for the S polarization, but also both branches violate the directional form of Kirchhoff's law.

4. Directional Kirchhoff's Law Violation

Returning to the equilibrium condition that Eq. (8) is equal to Eq. (9), one can perform a calculation for the enclosure in this configuration that is related to the directional form of Kirchhoff's law. This has been done in many studies, but it is worth reviewing in the present context. Equating Eqs. (8) and (9) gives

$$\varepsilon(\theta_j, \phi_j) = 1 - \int_{2\pi} f(\theta_i, \phi_i; \theta_j, \phi_j) \mathrm{d}\Omega_i. \quad (19)$$

Similarly, we can show that

$$\alpha(\theta_j, \phi_j) = 1 - \int_{2\pi} f(\theta_j, \phi_j; \theta_i, \phi_i) \mathrm{d}\Omega_i. \quad (20)$$

When the argument presented by Nicodemus[17] is followed, Eq. (19) shows that from only a thermodynamic basis, the emissivity toward a direction is the complement of the hemispherical-directional reflectance toward that direction. Thus we have shown that $\varepsilon(\theta_j, \phi_j) = 1 - \rho(2\pi; \theta_j, \phi_j)$, where 2π denotes integration over the hemisphere. But this is not the widely used relation for the measurement of emissivity by an integrating sphere, which is based on directional-hemispherical reflectance, $\varepsilon(\theta_j, \phi_j) = 1 - \rho(\theta_j, \phi_j; 2\pi)$. That relation is derived when one combines the relation for the absorptivity [Eq. (20)] and a connection between the directional emissivity and absorptivity that is the more powerful form of Kirchhoff's law,

$$\varepsilon(\theta_j, \phi_j) = \alpha(\theta_j, \phi_j), \quad (21)$$

which from Eqs. (19) and (20) requires that

$$\int_{2\pi} f(\theta_i, \phi_i; \theta_j, \phi_j)\mathrm{d}\Omega_i = \int_{2\pi} f(\theta_j, \phi_j; \theta_i, \phi_i)\mathrm{d}\Omega_i. \quad (22)$$

But we cannot say that these integrals are equal on the basis of thermodynamic laws. From Eq. (22) we see that Eq. (21) is in fact true if the BRDF is reciprocal, which applies for the majority of materials. But, based on our Faraday isolator example in Fig. 3, $\varepsilon(\theta_j, \phi_j) = \alpha(\theta_j, \phi_j)$ might not hold when the BRDF is not reciprocal, in other words, when time-reversal invariance does not apply. On one side of the surface, the structure is absorbing both polarizations and emitting only one of them, the other polarization is compensated by reflected light in an equilibrium situation. So, as with reciprocity, the directional form of Kirchhoff's law can be violated. It is not demonstrable from conservation-of-energy considerations. On the other hand, reciprocity holds for a general class of materials that are invariant under time reversal, so we have shown that indeed $\varepsilon(\theta_j, \phi_j) = \alpha(\theta_j, \phi_j)$ also holds for these materials.

5. Discussion

So, to be precise, for materials that are invariant under time reversal we have for the BRDF the reciprocal relation

$$f(\lambda, \varphi; \theta_i, \phi_i; \theta_j, \phi_j) = f(\lambda, \varphi; \theta_j, \phi_j; \theta_i, \phi_i), \quad (23)$$

where λ is the wavelength and φ represents the corresponding state of polarization. The BRDF is a property of the material only and the reciprocity relation holds under normal conditions with no restrictions on the illumination. If time reversal does not hold, reciprocity can be violated. In addition, we have assumed that the source and the detector are in the same medium. Although both reflection and transmission are reciprocal at the interface of nonconducting media, a transmission reciprocity violation can occur at the interface when at least one of the materials has a complex index of refraction, such as that for a metal.[11]

As for the directional form of Kirchhoff's law, assuming reciprocity and using some results from an enclosure calculation, we determined that

$$\varepsilon(\lambda, \varphi; \theta_j, \phi_j) = \alpha(\lambda, \varphi; \theta_j, \phi_j). \quad (24)$$

Although we derived this relation from the isothermal enclosure calculation, the directional emissivity and absorptivity are properties of the material. Although equilibrium is not required, there are some caveats for this expression that are explored extensively by Baltes.[21] First, in the regime in which there is significant stimulated emission, it must be treated as negative absorption. Otherwise, errors of more than 1% occur for $T\lambda > 3150$ K μm. Second, the system need not be in equilibrium with the surroundings, but its energy states must obey the equilibrium distribution. And third, emissivity is defined only when the surface or the structure has a unique temperature. For structures, this may not be the case, and the law can appear to be violated.[22]

There can also be apparent violations of these optical relations when they are averaged over wavelength or angle. Usually one wants to compute some band-averaged or angle-averaged radiometric quantity. It is best to do this computation by integration of the material properties together with the spectral, directional illumination. On the other hand, sometimes a derived optical property of a material such as the average reflectance across the solar spectrum, is more convenient for measurements or calculations. Derived properties involve the integration of spectral and angular properties. It is easy to show that these averaged properties and their relations can depend on the nature of the illuminating radiation. This is simply because the averaged property is the integral of an intrinsic property weighted by some assumed illumination conditions. For instance, integration of the directional absorptivity over the hemisphere (and the polarization) assumes that the absorptivity or the illumination or both are constant with angle. A table of the various directional and spectral combinations derived from Eq. (24) and the conditions of their applicability is presented by Grum and Becherer[23] and also by Siegel and Howell.[1] Relations of derived properties for which these types of restrictions apply include the spectral, hemispherical form of Kirchhoff's law, $\alpha(\lambda) = \varepsilon(\lambda)$, and the spectral, hemispherical conservation-of-energy law, $\alpha(\lambda) + \tau(\lambda) + \rho(\lambda) = 1$. Such laws hold only under the external conditions for which the integration over angle was valid.

6. Conclusions

Apparent violations of reciprocity and of Kirchhoff's law are sometimes seen in practice. For instance, in the laboratory, this is true for BRDF measurements of unusual materials.[24] [A. Springsteen, Labsphere, Inc., North Sutton, N.H. (personal communication)]. Such materials include effects paints, such as paints with metal flakes and layered optical materials. There are polarization effects and multiple reflections in such materials that may cause a critical dependence on some aspect of the measurement system. On the other hand, because there is no basis on fundamental thermodynamic laws, there is always the possibility of a nontrivial reciprocity violation.

In the field, radiometry and BRDF are applied extensively in remote sensing, and reciprocity violation is observed in measurements of natural land surfaces. Disparities of more than 10% occur in forest canopy data from Kimes[25] and from Deering[26] in which solar radiation is used for the source. These disparities are caused by various uncontrolled and uncorrected factors. The measurement, and even the definition of the BRDF for structures, depends on several geometric factors.[10] For instance, the surface sampling spot size must be large enough to average any variations, and the parallax and the edge effects of the spot must be negligible. Additional factors for remote-sensing field measurements include atmospheric effects, diffuse downwelling illumination, and temporal changes between measurements.[27]

In conclusion, neither the reciprocity of the BRDF nor the equivalence of the directional absorptivity and emissivity can be demonstrated by the conservation of energy in a thermodynamic enclosure calculation. On the other hand, these relations hold if the material or the structure is invariant under time reversal, which is usually true. So, for most materials, and in the absence of a strong magnetic field, it appears safe to assume the validity of BRDF reciprocity and the directional form of Kirchhoff's law.

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